

Replace the paragraph beginning at page 6, line 5 with the following rewritten paragraph:

a3 --A process is described in U.S. patents 4,629,607; 4,933,153; 5,063,032 and 5,389,355 to upgrade titania slag containing at least one alkaline earth impurity. Firstly the slag is preheated in a fluidized bed reactor in an atmosphere void of oxygen to prevent the oxidation of the Ti(III) present in the slag to Ti(IV). The slag is then contacted with hydrogen chloride gas. This results in the formation of iron and alkaline earth chlorides in the slag. Finally the chlorides that formed during the chlorination treatment are leached with either water or hydrochloric acid.--

Replace the paragraph beginning at page 8, line 1 with the following rewritten paragraph:

a4 09/744,531-061501 --Patent application PCT/CA96/00767 referred to in the above paragraph also stresses the differences between the treatment of ilmenite and titania slag. In example 12 the application illustrates that the process of GB1,225,826 relating to the treatment of ilmenite (as discussed above) is not suitable when applied to titania slag. As in the case of the process of PCT/CA96/00767, the process of GB1,225,826 includes an oxidation and subsequent reduction treatment. However, negligible removal of impurities are achieved when the process of GB1,225,826 is applied to slag, that is by oxidizing the slag with air at 850°C for 2 hours and then reducing it with smelter gas at 850°C for 5 minutes and thereafter leaching the resulting product with a hydrochloric acid solution under reflux conditions. Even if the process is modified by carrying out the oxidation at 900°C for 1 hour and the reduction at 900°C for 30 minutes (as set out in example 13 of PCT/CA96/00767) very poor results are achieved.--

Replace the paragraph beginning at page 8, line 19 with the following rewritten paragraph:

a5 --Most surprising it has now been found that if titania slag is oxidized at a lower temperature than that described in patent application PCT/CA96/00767 under the correct conditions and thereafter reduced and further treated, the slag can be suitably upgraded. In some embodiments of the invention it is not necessary to carry out the leaching at above atmospheric pressure. Leaching at a pressure above atmospheric pressure is required in the process of

a5 PCT/CA96/00767. It will be appreciated that even if leaching at above atmospheric pressure may not be necessary for the successful beneficiation of titania slag according to the invention, the process will also function if acid leaching is carried out at above atmospheric pressure.--

Replace the paragraph beginning at page 9, line 13 with the following rewritten paragraph:

--According to the present invention a method of treating titania slag to increase the leachability of the slag comprises the steps of

- sizing the titania slag to a particle size from 75 to 850  $\mu\text{m}$ ;
- oxidizing the sized slag particles in an oxidizing atmosphere at a temperature from about 700°C and above but below about 950°C for at least 30 minutes allowing the iron present in the slag to concentrate at the exposed surfaces of the slag particles, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) state; and
- reducing the oxidized slag in a reducing atmosphere from about 700°C to about 950°C for at least 5 minutes to convert a major portion of the iron in the Fe(III) state to the Fe(II) state without converting a substantial amount of the titanium in the Ti(IV) state to the Ti(III) state.--

Replace the paragraph beginning at page 10, line 3 with the following rewritten paragraph:

--According to another aspect of the present invention a method of treating titania slag to increase the leachability of the slag comprises the steps of

- sizing the titania slag to a particle size from 75 to 850  $\mu\text{m}$ ;
- oxidizing the sized slag particles in an oxidizing atmosphere at a temperature from about 700°C and above but below about 950°C for at least 30 minutes allowing an anatase phase to stabilize in the slag, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) stage; and

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- reducing the oxidized slag in a reducing atmosphere from about 700°C to about 950°C for at least 5 minutes, to convert a major portion of the iron in the Fe(III) state to the Fe(II) state and without converting a substantial amount of the titanium in the Ti(IV) state to the Ti(III) stage.--

Replace the paragraph beginning at page 11, line 3 with the following rewritten paragraph:

--During the oxidation step the iron present in the slag preferably concentrates at the exposed surfaces of the slag, and an anatase phase is allowed to stabilize in the slag.--

Replace the paragraph beginning at page 11, line 10 with the following rewritten paragraph:

--The oxidation is preferably carried out in a fluidized bed reactor.--

Replace the paragraph beginning at page 11, line 11 with the following rewritten paragraph:

--The oxidizing atmosphere may comprise oxygen diluted by an inert gas (preferably a mixture of CO<sub>2</sub> and N<sub>2</sub>) containing at least 2% oxygen by volume. More preferably the atmosphere results from the combustion of a carbonaceous fuel with excess air. Most preferably the oxidizing atmosphere contains between 4% and 8% oxygen by volume.--

Replace the paragraph beginning at page 11, line 15 with the following rewritten paragraph:

--Preferably more than 60%, preferably more than 75%, more preferably more than 90% and most preferably substantially all the iron in the Fe(II) state is converted to the Fe(III) state during oxidizing of the slag. The reduction is preferably carried out at a temperature between about 800°C and about 875°C.--

Replace the paragraph beginning at page 11, line 19 with the following rewritten paragraph:

--The reduction is preferably carried out in a fluidized bed reactor.--

a 10

Replace the paragraph beginning at page 12, line 11 with the following rewritten paragraph:

--According to another aspect of the invention there is provided a method of beneficiating titania slag to increase the  $\text{TiO}_2$  content thereof comprising the steps of:

- sizing the titania slag to a particle size from 75 to 850  $\mu\text{m}$ ;
- oxidizing the sized slag particles in an oxidizing atmosphere at a temperature from about 700°C and above but below about 950° for at least 30 minutes allowing the iron present in the slag to concentrate at the exposed surfaces of the slag particles, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) state;
- reducing the oxidized slag in a reducing atmosphere from about 700°C to about 950°C for at least 5 minutes to convert a major portion of the iron in the Fe(III) state to the Fe(II) state and without converting a substantial amount of the titanium in the Ti(IV) state to the Ti(III) state; and
- leaching the reduced slag with acid to obtain a beneficiated slag product with an increased  $\text{TiO}_2$  content and leach liquor containing the leached impurities.--

Replace the paragraph beginning at page 13, line 5 with the following rewritten paragraph:

--According to another aspect of the invention there is provided a method of beneficiating titania slag to increase the  $\text{TiO}_2$  content thereof comprising the steps of:

- sizing the titania slag to a particle size from 75 to 850  $\mu\text{m}$ ;
- oxidizing the sized slag particles oxidizing atmosphere at a temperature from about 700°C and above but below about 950°C for at least 30 minutes, allowing an anatase phase to stabilize in the slag, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) state;

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- reducing the oxidized slag in a reducing atmosphere from about 700°C to about 950°C for at least 5 minutes to convert a major portion of the iron in the Fe(III) state to the Fe(II) state and without converting a substantial amount of the titanium in the Ti(IV) state to the Ti(III) state; and
  - leaching the reduced slag with acid to obtain a beneficiated slag product with an increased TiO<sub>2</sub> content and leach liquor containing the leached impurities.--

Replace the paragraph beginning at page 15, line 11 with the following rewritten paragraph:

--Preferred embodiments of the invention will now be described by way of example only and with reference to the accompanying drawings wherein:

Figure 1 is a X-ray diffraction pattern of as-cast titania slag;

Figure 2 is a X-ray diffraction pattern of oxidized titania slag;

Figure 3 is a X-ray diffraction pattern of oxidized and reduced titania slag;

Figure 4 is a X-ray diffraction pattern of oxidized and reduced titania slag after leaching;

and

Figure 5 is a chemical composition profile through a titania slag particle oxidized for 1 hour at 850°C in 8% oxygen.

Replace the paragraph beginning at page 16, line 4 with the following rewritten paragraph:

--As described above titania slag is formed by smelting ilmenite ore in an electric arc furnace to form pig iron and titania rich slag. The titania rich slag is cast in a molten state into ladles whereby solid blocks are produced ranging from a few tons to as much as forty tons.

Titania slag mainly consists of a pseudobrookite solid solution phase also known as the M<sub>3</sub>O<sub>5</sub> solid solution. The solid solution phase with general formula (Fe<sup>2+</sup>, Mg<sup>2+</sup>, Mn<sup>2+</sup>, Ti<sup>4+</sup>, Ti<sup>3+</sup>)<sub>3</sub> O<sub>5</sub> contains iron in the Fe(II) state, titanium in the Ti(III) and (IV) states. Potentially it can also contain iron in the Fe(III) state but then titanium in the Ti(III) state will not be present.

Chemically the M<sub>3</sub>O<sub>5</sub> phase contains 81 to 91% TiO<sub>2</sub> and between 5% and 13% FeO. The M<sub>3</sub>O<sub>5</sub> phase occurs as fine to coarse grained, angular to sub-rounded greyish coloured particles with a

914  
smooth appearance. Small amounts of a silicate-rich glass can also be found, situated at the grain-and crystal boundaries of the individual  $M_3O_5$  crystals. This glass contains a second silicate-enriched glass. The silicate-enriched glassy phase has a smooth appearance and contains finely disseminated metallic iron spheroids and droplets. The major glassy phase is fine crystalline, containing fine needle-like titanium oxide crystallites as well as fine metallic iron particles and coarser-grained "globules". The larger metallic "globules" are characterized by an iron sulphide-containing outer rim. In most instances the slag may also contain small amounts of rutile.--

Replace the paragraph beginning at page 17, line 18 with the following rewritten paragraph:

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--The crushing and sizing of the titania slag is followed by an oxidation procedure. This is conducted by reacting the sized slag at a temperature between 700°C and 950°C, preferably between 800°C and 875°C with an oxidizing atmosphere for ½ to 4 hours. A fluid bed reactor is preferred for this procedure, while the oxidizing gas is preferably oxygen diluted by an inert gas (such as  $N_2$ ) to levels containing between 2% and 12%  $O_2$ .--

Replace the paragraph beginning at page 18, line 4 with the following rewritten paragraph:

916  
--An optical microscopic investigation conducted on polished blocks of the oxidized samples revealed that major changes in the general appearance, as well as mineralogical composition of the as-cast slag occurred during the oxidation process. Pores formed and slag particles lost their "smooth" appearance to become zoned. Some of the larger particles had unoxidized  $M_3O_5$  cores surrounded by a  $TiO_2$ -rich intermediate zone. Most of the smaller particles were transformed to  $TiO_2$ . The  $TiO_2$  phases that formed were a mixture of anatase and rutile. On the outside edges of all the particles were iron-enriched, slightly porous marginal zones. Figure 5 provides evidence of the iron enriched outside edge. Limited iron migration towards the edges of cracks also occurred. Inside the unoxidized  $M_3O_5$  cores of the slag particles fine metallic iron particle, situated at the edges of fine cracks extending through the slag

a16 particles, could be observed. Most of the iron is converted to the Fe(III) state and all of the titanium is present in the Ti(IV) state.--

Replace the paragraph beginning at page 19, line 5 with the following rewritten paragraph:

--Reduction of the oxidized titania slag

a17 The next step is to reduce the oxidized slag. This is conducted by contacting the oxidized slag particles with a reducing agent at a temperature from about 700°C to about 950°C, preferably between about 800°C and about 875°C, preferably in a fluidized bed reactor. The reduction is carried out for a period of at least 20 minutes.--

Replace the paragraph beginning at page 19, line 13 with the following rewritten paragraph:

a18 --The general optical appearance of the slag particles after reduction is very similar to those of the oxidized products except that the iron enriched outer rims of the particles are converted to ilmenite. Some of the particles can be coated with a thin layer of carbon. Most, but not all of the iron is converted to the Fe(II) state and only a very small portion of the titanium is converted to the Ti(III) state.--

Replace the paragraph beginning at page 19, line 19 with the following rewritten paragraph:

--A typical X-ray diffraction pattern of titania slag that was oxidized and reduced is presented in Figure 3. This shows:

i) a main rutile peak (r) at a d-spacing of 3.247Å and a 2θ angle of 27.445° for Cu Kα radiation;

a19 ii) a main anatase peak (a) taken at a d-spacing of 3.52Å and a 2θ angle of 25.279° for Cu Kα radiation;

iii) a minor ilmenite peak (i), taken at a d-spacing of 2.754Å and a 2θ angle of 32.483° for Cu Kα radiation; and

iv) a minor pseudobrookite peak (P) taken at a d-spacing of 3.483Å to 3.497Å and a 2θ angle from 25.553° to 25.449° for Cu Kα radiation.--

Replace the paragraph beginning at page 20, line 10 with the following rewritten paragraph:

Q 20 --After the oxidation and reduction roast the slag is leached in 20 wt% hydrochloric acid at the boiling point of the acid at atmospheric pressure or at elevated pressure. The solids are contacted with an excess of acid required to dissolve the iron and other impurity oxides. The time required for leaching will be dictated by the slag composition and the temperature used for the reaction. Optically, the leached residue displays a weathered appearance compared to the oxidized as well as reduced products. The effect of leaching is most prominent along the outer margins of the slag particles as well as along cracks extending into the individual slag particles.--

Q 21 Replace the paragraph beginning at page 22, line 9 with the following rewritten paragraph:

Q 21 --The slag was broken down by crushing and screened at +106  $\mu$ m-850  $\mu$ m. Following this the slag was oxidized in a fluidized bed reactor at 850°C for 30 minutes in an oxidizing atmosphere comprising a mixture of air and carbon dioxide that set the oxygen level at 8%. Thereafter it was reduced in the same reactor at 850°C for 20 minutes in a reducing atmosphere comprising chemically pure carbon monoxide. The roasted slag was then leached in boiling 20% hydrochloric acid at atmospheric pressure for 12 hours. At the conclusion of the leach procedure the leach solution was decanted and the solids were washed and dried at 150°C. The composition of the beneficiated titania slag is given in Table 4.--

Replace the paragraph beginning at page 23, line 4 with the following rewritten paragraph:

Q 22 --The same slag as in Example 1 was broken down by crushing and screened at +106  $\mu$ m-850  $\mu$ m. Following this the slag was oxidized in a fluidized bed reactor at 950°C for 120 minutes in an oxidizing atmosphere comprising a mixture of air and carbon dioxide that set the oxygen level at 8%. Thereafter it was reduced in the same reactor at 950°C for 20 minutes in a reducing atmosphere comprising chemically pure carbon monoxide. The roasted slag was then leached in boiling 20% hydrochloric acid at atmospheric pressure for 12 hours. At the conclusion



a22 of the leach procedure the leach solution was decanted and the solids were washed and dried at 150°C. The composition of the beneficiated titania slag is given in Table 5.--

Replace the paragraph beginning at page 24, line 3 with the following rewritten paragraph:

--The slag was broken down by crushing and screened at +106  $\mu$ m-850  $\mu$ m. Following this the slag was oxidized in a fluidized bed reactor at 850°C for 120 minutes in an oxidizing atmosphere comprising a mixture of air and carbon dioxide that set the oxygen level at 12%. Thereafter it was reduced in the same reactor at 850°C for 20 minutes in a reducing atmosphere comprising chemically pure carbon monoxide. The roasted slag was then leached in boiling 20% hydrochloric acid at atmospheric pressure for 12 hours. At the conclusion of the leach procedure the leach solution was decanted and the solids were washed and dried at 150°C. The composition of the beneficiated titania slag is given in Table 7.--

Replace the paragraph beginning at page 24, line 14 with the following rewritten paragraph:

--The same slag as in Example 1 was broken down by crushing and screened at +106  $\mu$ m-850  $\mu$ m. Following this the slag was oxidized in a fluidized bed reactor at 705°C for 120 minutes in an oxidizing atmosphere comprising a mixture of air and carbon dioxide that set the oxygen level at 4%. Thereafter it was reduced in the same reactor at 750°C for 20 minutes in a reducing atmosphere comprising chemically pure carbon monoxide. The roasted slag was then leached in boiling 20% hydrochloric acid at atmospheric pressure for 12 hours. At the conclusion of the leach procedure the leach solution was decanted and the solids were washed and dried at 150°C. The composition of the beneficiated titania slag is given in Table 8.--

Replace the paragraph beginning at page 26, line 8 with the following rewritten paragraph:

--The slag was broken down by crushing and screened at +106  $\mu$ m-850  $\mu$ m. Following this the slag was oxidized in a fluidized bed reactor at 850°C for 3 hours in an oxidizing atmosphere that resulted from the combustion of coal char in an excess of air. Thereafter it was reduced in the same reactor at 800°C for 30 minutes in a reducing atmosphere that resulted from